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The determination of Gibbs energy of the exchange reaction of sulphides using beta-alumina solid electrolyte

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EMF measurements of the cell Na(l) | β''-alumina | Na_2S + Ag_2S + Ag were carried out in the temperature range of 463.4 to 843.7 K. The results were represented by the equation $E/V(\pm 0.00057) = 1.75793(\pm 0.00086) - 4.452(\pm 0.014) \times 10^{-4}(T)$ where $463.4 < T < 737.7$ K. The Gibbs energy of the exchange reaction $\frac{1}{2}Ag_2S(s) + Na(l) \rightarrow \frac{1}{2}Na_2S(s) + Ag(s)$ was determined from the EMFs. The standard Gibbs energy of formation of Na_2S in the reaction $2Na(l) + \frac{1}{2}S_2(g) = Na_2S(s)$ was obtained from the values of EMF and $\Delta G^0_{Ag_2S}$ in the literature as $\Delta G^0_{Na_2S}(J\,mol^{-1} \pm 1160) = -427940 + 124.92T$ where $463.4 < T < 737.7$ K. The eutectic temperature of the Ag_2S–Na_2S system was estimated to be 738 ± 5 K.

1. Introduction

Beta-alumina (β-, β''-alumina) solid electrolyte is an Na^+ superionic conductor and is available for various investigations of materials in the temperature range from room temperature to 1700 K. When the EMF method using beta-alumina is applied to determine the thermodynamic properties, the measurement of the equilibrium EMF is possible even in the vicinity of room temperature in the case where the mass transfer in the electrode materials is fairly fast. In our previous paper [1], the Gibbs energy of formation of AgI was determined by EMF measurements of the following galvanic cell from room temperature to 647 K:

$$Na(s, l) | \beta''\text{-alumina} | NaI + AgI + Ag$$

Therefore, it is possible to determine the thermodynamic properties of various kinds of material at lower temperatures when a superionic conducting material is used as the electrode material. Based on this principle, the Gibbs energy of the exchange reaction

$$Pb + Ag_2S = 2Ag + PbS$$

was also determined by the EMF method using the galvanic cell [2]

$$Pb(s, l) | Pb^{2+}\text{-}\beta''\text{-alumina} | PbS + Ag_2S + Ag$$

in the temperature range above 411 K.

In this study, EMF measurement of the galvanic cell

$$Na(l) | \beta''\text{-alumina} | Na_2S + Ag_2S + Ag$$

was carried out and the Gibbs energy of exchange reaction of the reaction

$$\tfrac{1}{2}Ag_2S(s) + Na(l) \rightarrow \tfrac{1}{2}Na_2S(s) + Ag(s) \quad (1)$$

were determined from the EMFs.

2. Experimental procedure

Mixtures of Ag, Ag_2S and Na_2S were prepared by mixing silver powder of 3N purity, Ag_2S powder of 5N purity, and Na_2S powder of 3N purity in molar ratios of 1.00 : 1.00 : 1.00 for Run 1 and 3.00 : 3.00 : 1.00 for Run 2. Total weights of the mixed powders were 3.565×10^{-3} and 4.643×10^{-3} kg for Runs 1 and 2, respectively. A β''-alumina crucible was used as a solid electrolyte which was supplied by the NGK Spark Plug Company Ltd. The dimensions of the crucible were 15 mm o.d., 13 mm i.d. and 120 mm height. The cell assembly was almost the same as that used in the previous paper [1]. 3×10^{-3} kg of sodium of 3N purity was used as a reference electrode. Silver wire and iridium wire spot-welded to Kanthal wire were used as the lead in the cathode for Runs 1 and 2, respectively. Molybdenum wire was used as the lead in the anode. EMF values were corrected for the thermoelectromotive force between the leads. After assembling the cell, the system was evacuated at 373 K for 80 ksec. Purified argon was then introduced into the system, and the system was heated to the first planned temperature. The cell system was kept in a Nichrome wire-wound furnace with a constant-temperature zone of ±0.5 K of 80 mm at 573 K. The temperature of the furnace was controlled to ±0.3 K by a proportional controller with a Pt/Pt–13% Rh thermocouple. The temperature of the cell was measured independently by another Pt/Pt–13% Rh thermocouple. The open-circuit EMF of the cell was measured by a Yokogawa 2502A digital multimeter with an input impedance of more than 1000 MΩ. The EMF that remained within ±0.1 mV for longer than 8 ksec at a constant temperature was regarded as an equilibrium EMF at that temperature. The measurement of the EMF in one experimental run was carried out for longer than one month.

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TABLE I List of the experimental results

Data No.	T(K)	E/V	ΔG* (J mol^{-1})	ΔG_{Na_2S}† (J mol^{-1})
Run 1				
1	625.8	1.4785	−142650	−349570
2	677.9	1.4560	−140480	−343240
3	727.3	1.4343	−138390	−337160
4	562.0	1.5077	−145470	−357710
5	617.4	1.4835	−143130	−350850
6	646.7	1.4702	−141850	−347170
7	691.2	1.4502	−139920	−341610
8	748.8	1.4232	−137320	
9	664.5	1.4620	−141060	−344910
10	618.6	1.4825	−143040	−350610
11	584.6	1.4980	−144530	−354930
12	550.6	1.5129	−145970	−359170
13	529.8	1.5220	−146850	−361760
14	501.4	1.5351	−148110	−365430
15	463.6	1.5533	−149870	−370460
16	521.8	1.5248	−147120	−362630
17	569.5	1.5038	−145090	−356660
18	600.0	1.4902	−143780	−352810
19	638.4	1.4735	−142170	−348120
20	696.4	1.4478	−139690	−340950
21	716.5	1.4389	−138830	−338460
22	762.3	1.4124	−136270	
23	808.7	1.3869	−133810	
24	843.7	1.3765	−132810	
25	825.0	1.3818	−133320	
26	794.4	1.3923	−134340	
27	778.1	1.3989	−134970	
28	756.0	1.4175	−136770	
29	737.7	1.4299	−137960	−335920
30	680.1	1.4558	−140460	−343110
31	617.9	1.4832	−143110	−350780
32	542.4	1.5174	−146410	−360370
33	790.9	1.3926	−134360	
34	791.4	1.3769	−132850	
35	782.2	1.3889	−134010	
36	804.0	1.3546	−130700	
Run 2				
1	767.3	1.4325	−138210	
2	785.9	1.4382	−138760	
3	739.6	1.4281	−137790	
4	700.2	1.4464	−139560	−340530
5	671.7	1.4590	−140770	−344050
6	652.6	1.4675	−141590	−346420
7	634.9	1.4751	−142320	−348560
8	610.9	1.4858	−143360	−351540
9	596.0	1.4924	−143990	−353390
10	555.9	1.5089	−145590	−358190
11	753.2	1.4285	−137830	
12	773.4	1.4330	−138260	
13	810.1	1.4490	−139810	
14	827.6	1.4575	−140630	
15	825.7	1.4396	−138900	
16	758.9	1.4303	−138000	
17	712.3	1.4412	−139050	−339070
18	584.0	1.4979	−144520	−354940
19	511.2	1.5299	−147610	−364040

*Calculated from $\Delta G = -FE$, $F = 96484.56\,\mathrm{C\,mol^{-1}}$.

†Calculated from ΔG and $\Delta G^0_{Na_2S}$ value in Table II.

3. Results and discussion

The open-circuit EMF of Cell I, E, is related to the Gibbs energy change of Equation 1 by

$$\Delta G = -FE = \tfrac{1}{2}(\Delta G^0_{Na_2S} - \Delta G^0_{Ag_2S}) + RT\ln\{[a_{Na}(a_{Ag_2S})^{1/2}]/[a_{Ag}(a_{Na_2S})^{1/2}]\} \tag{2}$$

where E is the EMF in volts, F the Faraday constant, $\Delta G^0_{Na_2S}$ and $\Delta G^0_{Ag_2S}$ the standard Gibbs energies of formation of Na_2S and Ag_2S, and a_i is the activity of component i.

When the cell temperature was raised to the first planned temperature in Run 1, an equilibrium EMF was obtained within two days. In Run 2, equilibrium EMF was not obtained after one week below 738 K, and the equilibrium value was obtained by increasing the temperature above 738 K. The experimental results are listed in Table I and shown in Fig. 1. Although the phase diagram for a Ag_2S–Na_2S has not been reported, the eutectic temperature of the system is estimated to be 738 ± 5 K from the experimental results. By the least-squares method for the data below 737.7 K, the data were represented by the linear relationship between EMF and temperature

$$E/V(\pm 0.00057) = 1.75793(\pm 0.00086) - 4.452(\pm 0.014) \times 10^{-4}(T) \tag{3}$$

where $463.4 < T < 737.7$ K. An equilibrium EMF could not be obtained below the α–β transformation temperature of Ag_2S, $T_t = 449$ K.

Using Equations 2 and 3, one obtains

$$\Delta G(\mathrm{J} \pm 55) = -169613(\pm 83) + 42.95(\pm 0.13)(T) \tag{4}$$

The broken line in Fig. 1 represents the calculated value for Equation 2 using the G values in Table II [3, 4] and substituting unity for all the activities. $\Delta G^0_{Na_2S}$ for the reaction

$$2\mathrm{Na(l)} + \tfrac{1}{2}\mathrm{S_2(s)} \rightarrow \mathrm{Na_2S(s)} \tag{5}$$

was calculated using the experimental EMFs and $\Delta G^0_{Ag_2S}$ values in Table II for the reaction

$$2\mathrm{Ag(s)} + \tfrac{1}{2}\mathrm{S_2(g)} \rightarrow \mathrm{Ag_2S(s)} \tag{6}$$

The results are shown in Fig. 2 and Table I. $\Delta G^0_{Na_2S}$ is given by

$$\Delta G^0_{Na_2S}(\mathrm{J\,mol^{-1}} \pm 130) = -427940(\pm 200) + 124.92(\pm 0.32)(T) \tag{7}$$

TABLE II Thermochemical data of G values [3, 4] used in this study

T(K)	G(J mol^{-1})					ΔG^0(J mol^{-1})	
	S_2(g)	Na(l)	Ag(s)	Na_2S(s)	α-Ag_2S(s)	Na_2S(s)	Ag_2S(s)
500	12736	−28192	−22790	−419053	−108474	−369037	−69262
600	−12163	−35869	−28644	−432236	−128616	−354416	−65247
700	−37664	−44049	−34945	−446880	−150151	−339950	−61429

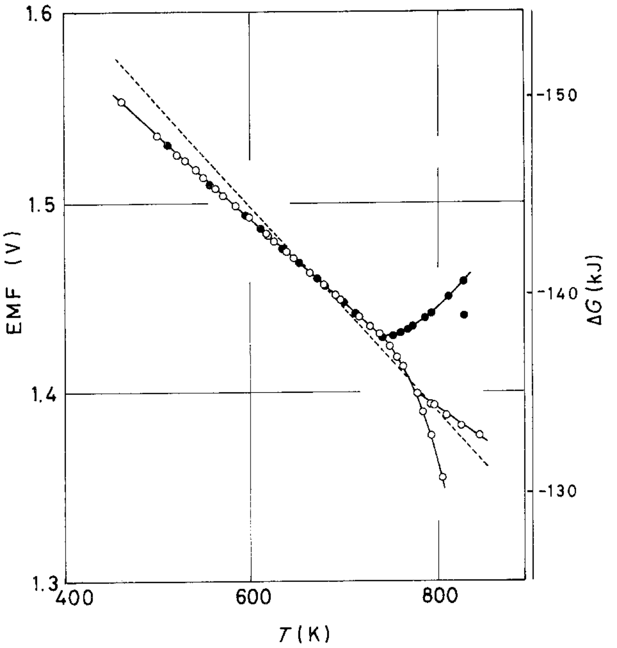

Figure 1 EMF of the cell Na(l) | β''-alumina | Na_2S + Ag_2S + Ag. (○)Run 1, (●)Run 2, (– – –) calculated from the thermochemical data of Barin and co-workers [3, 4].

where $463.4 < T < 737.7$ K. Additional uncertainties are those associated with the thermochemical quantities involved in the calculations. For example, the uncertainty in $\Delta G^0_{Ag_2S}$ values is $\pm 1150\,J\,mol^{-1}$. The overall uncertainty in $\Delta G^0_{Na_2S}$ was derived by obtaining the square root of the sum of the squares of the uncertainty from these measurements, $\pm 130\,J\,mol^{-1}$, and the uncertainty in $\Delta G^0_{Ag_2S}$ of $\pm 1150\,J\,mol^{-1}$, to yield $1160\,J\,mol^{-1}$. The $\Delta G^0_{Na_2S}$ values calculated from Table II are represented by

$$\Delta G^0_{Na_2S}(J\,mol^{-1}) = -441729 + 145.44(T) \qquad (8)$$

where $500 < T < 700$ K. The maximum uncertainty in the $\Delta G^0_{Na_2S}$ value [3, 4] is $\pm 5700\,J\,mol^{-1}$ between 500 and 700 K. The results are compared in Fig. 2. The differences in the $\Delta G^0_{Na_2S}$ values between Equations 7 and 8 are 2450 and $500\,J\,mol^{-1}$ at 500 and 700 K, respectively.

In Run 1 the EMFs did not lie on the straight line given by Equation 3 above 738 K, as shown in Fig. 1. The EMFs above 738 K were located in the region between the two curves. This is attributed to the appearance of a liquid sulphide phase. The upper and lower curves in Fig. 1 would correspond to the three-phase mixture of Ag + Ag_2S + liquid $(Ag–Na)_2S$ and Ag + Na_2S + liquid $(Na–Ag)_2S$, respectively, where liquid $(Ag–Na)_2S$ and $(Na–Ag)_2S$ represent, respectively, the liquid phases on the liquidus line in the Ag_2S side and the liquid phase on the liquidus line in the Na_2S side in the Ag_2S–Na_2S eutectic system. In Run 1, the EMFs above 738 K lay on the lower curve (Nos 8, 22, 28 in Table I) and a straight line (Nos 23, 24, 25, 26, 27, 33). The straight line would correspond to the two-phase mixture of Ag + liquid-$(Na–Ag)_2S$. After the EMFs of No. 33 were measured, sodium was coulometrically titrated to the cathode by an amount 300 C. Then EMFs of 1.3769 V (No. 34) was reached. The EMFs of Nos 34, 35 and 36 lay on the curve represented by Nos 8, 22 and 28.

In Run 2, when the cell temperature was kept at higher temperatures above 738 K where the liquid sulphide phase appears, an ion-exchange reaction proceeded between the Na^+ ion in the β''-alumina crucible and the Ag^+ ion in the liquid phase. When ion exchange occurs, sodium is introduced into the $(Ag–Na)_2S$ phase and silver is introduced into the β''-alumina crucible. This causes an increase in the amount of Na_2S in the melt. The decrease in the EMF value of No. 14 of 1.4575 V at 827.6 K, to No. 15 of 1.4395 V at 825.7 K, correspond to a transfer from the three-phase mixture of Ag + Ag_2S + liquid $(Ag–Na)_2S$ to the two-phase mixture of Ag + liquid $(Ag–Na)_2S$. An ion exchange reaction has also been observed between a β''-alumina crucible and a liquid iodide phase [5].

4. Conclusion

EMF measurements of the cell

$$Na(l) \,|\, \beta''\text{-alumina} \,|\, Na_2S + Ag_2S + Ag$$

were carried out in the temperature range of 463.4 to 843.7 K. The results were represented by

$$E/V(\pm 0.00057) = 1.75793(\pm 0.00086) - 4.452(\pm 0.014) \times 10^{-4}(T)$$

where $463.4 < T < 737.7$ K. The Gibbs energy of the exchange reaction

$$\tfrac{1}{2}Ag_2S(s) + Na(l) \rightarrow \tfrac{1}{2}Na_2S(s) + Ag(s)$$

was represented by

$$\Delta G(J \pm 55) = -169613(\pm 83) + 42.95(\pm 0.13)(T)$$

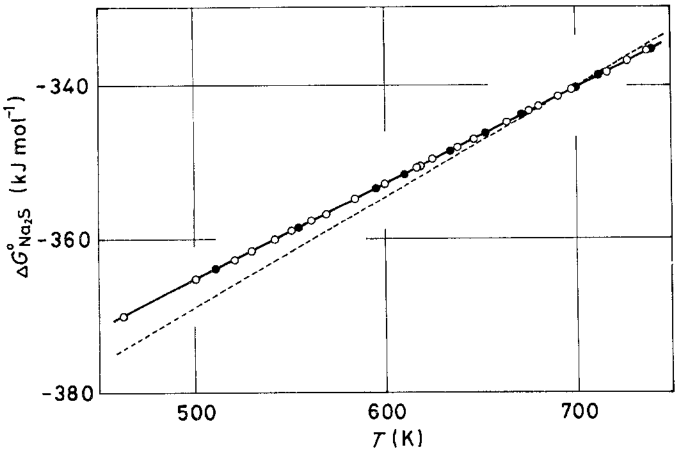

Figure 2 Comparison of the values for $\Delta G^0_{Na_2S}$ for the reaction $2Na(l) + \frac{1}{2}S_2(g) = Na_2S(s)$. (○)Run 1, (●)Run 2, (– – –) calculated from the thermochemical data of Barin and co-worders [3, 4].

The standard Gibbs energy of formation of Na_2S in the reaction

$$2Na(l) + \frac{1}{2}S_2(g) = Na_2S(s)$$

was obtained from the EMFs and $\Delta G^0_{Ag_2S}$ values calculated from the thermochemical data by Barin and co-workers [3, 4] and given by

$$\Delta G^0_{Na_2S}(\mathrm{J\,mol^{-1}} \pm 1160) = -427940 + 124.92(T)$$

where $463.4 < T < 737.7\,\mathrm{K}$. The eutectic temperature of the Ag_2S–Na_2S system was estimated to be 738 ± 5 K.

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